

Modeling of Ni²⁺ exchange on the strong acid ion-exchange resin and the organic-inorganic ionite

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Abstract – In dynamic conditions extraction of ions of Ni²⁺ from the combined solution with using of acid ion-exchange gel pitch and the composite ionite on its basis containing units of nanoparticles of hydrophosphate of zirconium is investigated. The model allowing to define time for which capacity of Ni²⁺ ions is fulfilled. The model assumes use only of empirical parameters reflecting concoction of ions in a firm phase.

Key words – ion exchange treatment of water, the nickel ions, calcium, magnesium, dynamic model.

I. Introduction

Along with reverse osmosis, ion exchange, conventionally used for a wide range of practical problems, such as desalination of water [1], in particular, seawater [1, 2], an extract from the waste water of toxic and the ionic components [3, 4] cleaning liquid food products, the concentration of ions for subsequent analytical determination and many others. For the calculation of processes in ion-exchange columns is typically used bulky models that involve the use of such parameters as the diffusion coefficients of the ions in solution and ion exchanger, the exchange capacity of the latter, the coefficients of selectivity, the particle size of the resin layer and the height, the speed of solution. The greatest difficulty is the definition of the diffusion coefficient of exchanging ions in the ion exchanger, as this parameter varies with the degree of substitution of the resin and is very dependent on the presence of other ions in solution, which are absorbed by the ion exchanger as an exchange, and on nonexchange mechanism. When determining the ratio of selectivity also has problems if the solution contains several types of ions of the same sign of charge as well as the incomplete dissociation of the functional groups. In this regard, an actual problem is formalized model creation process in the dynamic mode, which minimizes the number of parameters, eliminating the diffusion coefficients and selectivities.

II. The experimental procedure

The purpose of research - the creation of a formalized model of ion exchange, only with empirical parameters. To achieve this goal it is necessary to solve such problems:

1. Ion-exchange extraction of Ni²⁺ ions from a solution also containing hardness ions, by ion exchange resins, and organic-inorganic ion exchanger.

2. To establish a correlation between the concentration of Ni²⁺ ions in solution and the exchange capacity of ion exchangers breakthrough.

3. Determine the empirical model parameters for different ion exchangers.

Investigated the strongly acidic gel anionite Dowex HCR-S (Dow Chemical) with the following characteristics: exchange capacity (Na⁺) – 2.4 mmol cm⁻³, the water content – 60% decrease in the translation of the H in the form of Na-substituted – 8%. Ion modified aggregates of nanoparticles of zirconium hydrogen phosphate, modification consisted of impregnation of the resin insoluble hydrogen zirconium and subsequent deposition in the polymer matrix of zirconium hydrogen phosphate (ZHP) solution H₃RO₄ similarly. As was established by using scanning and transmission microscopy, the size of the aggregates is prevailing several microns (Fig. 1) consisted of aggregates of nanoparticles (10-15 nm). The content of the modifier in the composite ion exchanger was 22 wt% water content – 58% on transfer-substituted form of Na⁺ ion exchanger volume decreased 1.5 times.

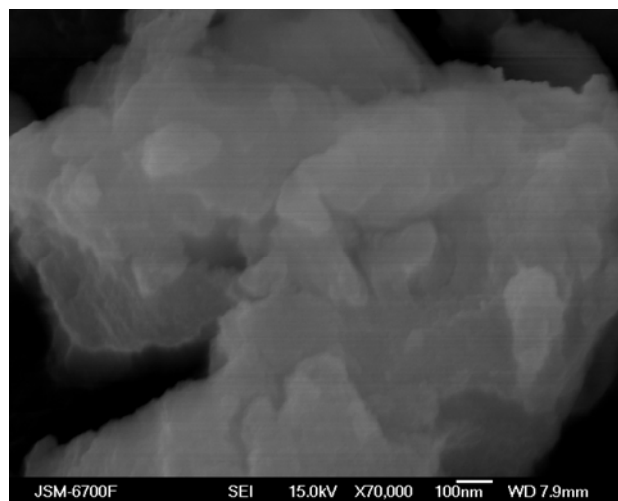


Fig. 1. Zirconium hydrogen phosphate

Ion content in the outlet of the column was determined by atomic absorption method using the device S9 Pye Unicam (Philips).

III. Results of the study

Fig. 2 illustrates a typical output curves ions Ni²⁺, obtained for the polymer and organic-inorganic ion exchanger according – ion concentration at the column outlet from the volume of solution passed. The curves show the wide plateau and the rise of responsible container before breakthrough of the ion exchanger (mmol cm⁻³) – this value, depending on the process conditions (composition of the solution and its

speed, the geometric parameters of the bulk layer) corresponds to a degree of substitution of the resin, in which the maximum degree extraction of certain ions from a solution is not implemented.

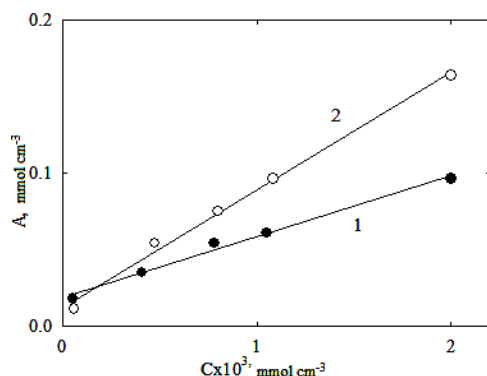


Fig. 2. The exchange capacity before breakthrough at cations Ni^{2+} cation exchange resin (1) and organic-inorganic ion exchanger (2) as a function of the initial content of these ions in solution

In other words, the introduction of inorganic modifier ZHF in strongly acidic ion exchanger resin enhances the ability to concentrate Ni^{2+} ions in the presence of hardness ions. Since the ion-exchange resins, modified nanoparticle aggregates ZHF, characterized by lower mobility of adsorbed ions and exchange capacity, improvement of the sorption capacity of the composites is obviously due to the peculiarities of ion exchange on the ZHF. Previously, it was found that the exchange of $\text{Ni}^{2+} \rightarrow \text{H}^+$ using ZHF accompanied by partial hydrolysis $\text{Ni}^{2+} \rightarrow \text{NiOH}^+$ ions sorbed directly into the ion exchanger phase (in a neutral solution forms NiON^+ content is very low). Ni^{2+} ions and NiON^+ form complexes with a phosphate functional groups. Probably complexes with these cations are more stable than the hardness ions, which causes preferential absorption of toxic ions composite.

Capacity before breakthrough was calculated by the formula:

$$A = \frac{(C - C_f)V}{v} \quad (1)$$

where C and C_f – ion concentration in the solution at the inlet and outlet of the column (mmol cm^{-3}), V – volume of the solution (cm^3), v – the amount of the resin (cm^3).

Dependences A of the initial concentration of Ni^{2+} described by linear polynomials:

$$A = a_1C + a_0, \quad (2)$$

where a – empirical coefficients, a_0 – exchange capacity of the ion exchanger, achieved an infinitesimal ion content in solution (mol cm^{-3}), a_1 – factor reflecting the concentration of Ni^{2+} in the solid phase (dimensionless). Which a_1 can be regarded as analogous to the distribution coefficient, which is determined under static conditions. The coefficients a_0 , obtained for unmodified and organic-inorganic ion exchangers, are very similar (0.018 and 0.012 mmol cm^{-3} , respectively), while the values of a_1 are 40 and 77 respectively.

For unmodified cation exchange resin model ($A-V/U$) is inverse polynomial of the first order

$$A = \frac{b_1v}{V} + b_0 \quad (3)$$

where b_0 – capacity of ion exchanger. For organic-inorganic ion exchanger:

$$A = \frac{b_2v^2}{V^2} + \frac{b_1v}{V} + b_0 \quad (4)$$

Equating the expressions (2) and (3), we obtain the relation in which the capacity will be reached before breakthrough unmodified ion exchanger:

$$\frac{V}{v} = \frac{b_1}{a_1C + a_0 - b_0} \quad (5)$$

For organic-inorganic ion exchanger equating equations (2) and (4) provides:

$$\frac{b_2v^2}{V^2} + \frac{b_1v}{V} + b_0 = a_1C + a_0 \quad (6)$$

Solve the equation with respect to V/U , we obtain:

$$\frac{V}{v} = \frac{-b_1 \pm \sqrt{b_1^2 - 4b_2(b_0 - a_1C - a_0)}}{2(b_0 - a_1C - a_0)} \quad (7)$$

Studies are an extension of our ongoing work, dedicated to the production of organic-inorganic ion-exchange materials and study their functional properties. In this study we compared the cation exchange resin and organic-inorganic ion exchanger resin based on this modified zirconium hydrogen phosphate. In the study of ion exchange extraction of Ni^{2+} from the combined solutions containing hardness ions, the mathematical model, varying the parameters of which are the concentration of extractable ions, as well as the ratio of the maximum volume of the solution, at which the capacity to slip, and the resin. Correlation equations to determine the capacity of the ion exchangers to slip without prior determination of the coefficients of selectivity and diffusion of adsorbed ions, as well as the mode of exchange. This model is advantageous because the mode determination process, and these characteristics of ion exchangers, requires a large array of experimental data that can not always be adequately interpreted, especially when removing ions from a multicomponent solution. The coefficients of correlation equations allow you to compare different resins.

The resulting model after verification, these additions in the future may be used for the calculation of ion exchange and sorption processes to extract from the combined solution of a component.

Conclusion

This model involves the use of only empirical parameters obtained in the investigation of ion exchange in a dynamic mode and does not require a predetermined ratio of selectivity and the diffusion of sorbed ions, and the exchange mode.

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